

Complex ion formation in liquid Ag-Se alloys

F. Kirchhoff, J. M. Holender and M. J. Gillan

Physics Department, Keele University

Keele, Staffordshire ST5 5BG, U.K.

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Abstract

Ab initio molecular dynamics simulations are used to investigate the structure and electronic properties of the liquid Ag-Se system at three compositions. The realism of the simulations is demonstrated by comparison with diffraction data for the stoichiometric case Ag_2Se . As the Se content is increased beyond the stoichiometric value, short-lived Se_n complexes are formed. The concentration of complexes and the associated changes of electronic structure can be explained using a simple ionic model.

61.20Ja, 61.20.-p, 61.20.Gy, 71.55.Ak

Many binary liquids show a dramatic dependence of their structure and electronic properties on composition [1]. A celebrated example is the Cs-Au system, in which the pure elements are excellent metals, but nevertheless the equiatomic mixture has a very low conductivity and a structure characteristic of a molten salt [2]. These effects arise from the electronegativity difference between the elements, and the resulting charge transfer, partial ionicity and atomic ordering. In systems where one of the elements is a semiconductor in the liquid state – for example alloys of metals with S or Se – even richer behavior can be expected, since variation of composition should change the bonding from metallic through partially ionic to covalent. We report here a set of simulations of the Ag-Se system performed using *ab initio* molecular dynamics (AIMD), which we have used to explore these effects.

The Ag-Se system has been studied by a variety of experimental techniques [3], but understanding of its structure is limited, since diffraction measurements have been made only near the stoichiometric composition Ag_2Se [4], and these yield only the *total* structure factor and not the partial correlations between the two elements. The present simulations allow us to build up a detailed picture of the composition-dependent structure, and also give important new insights into the electronic structure and into dynamical aspects of the bonding, which would be hard to probe experimentally. A number of previous AIMD simulations of liquid metals and semiconductors have been reported [5], but the Ag-Se system presents a significant technical challenge, as will become clear.

We shall show that our simulations are in excellent agreement with available structural measurements at the stoichiometric composition Ag_2Se , where we find that a partially ionic description is appropriate. As soon as the Se content is increased beyond the stoichiometric value, a major structural change begins, consisting of formation of Se_n complexes. This is accompanied by changes of the electronic density of states (DOS) associated with the formation of covalent Se-Se bonds. Both the concentration of Se_n complexes and the changes in the DOS can be understood using a simple ionic model. In spite of their major structural role, the complexes turn out to be surprisingly short-lived, the typical bond lifetime being

~ 0.5 ps.

Our AIMD technique, like the methods pioneered by Car and Parrinello [6], uses density functional theory, pseudopotentials, and a plane-wave representation of the orbitals [7]. However, instead of treating the electronic degrees of freedom as fictitious dynamical variables, we use conjugate-gradient minimization [8] to reach the self-consistent ground state at each step. The Hellmann-Feynman forces are then used to integrate the classical equation of motion of the ions. To handle the semi-metallic nature of the system, we use Fermi-surface smearing, with the electronic occupation numbers treated as auxiliary dynamical variables [9–11].

The details of our calculations are as follows. We use *ab-initio* norm-conserving non-local pseudopotentials, with exchange and correlation included *via* the local density approximation in Ceperley-Alder form [12]. The Ag pseudopotential has been optimized using the method of Lin *et al.* [13], which is a refinement of the scheme due to Rappe *et al.* [14]. The Se pseudopotential does not require optimization and the standard Kerker method [15] suffices. The *s* and *p* components of the Ag pseudopotential were generated using the atomic configuration $4d^{10} 5s^{0.25} 5p^{0.25}$, and the *d* component using the configuration $4d^{10} 5s^{0.5}$. The core radii were 2.0, 2.0 and 2.5 a.u. for the *s*, *p* and *d* components respectively. For Se we used $4s^2 4p^4$ for the *s* and *p* waves and $4s^2 4p^{2.75} 3d^{0.25}$ for the *d* wave; the core radii for were chosen to be 2.0, 2.0, and 2.3 a.u. for the *s*, *p* and *d* components respectively. We use the pseudopotentials in Kleinman-Bylander separable form [16] with the *s*-wave treated as local; the non-local parts of the pseudopotentials are treated in real space [17]. Tests on the low-temperature crystal phase of Ag_2Se show that these pseudopotentials reproduce the experimental structure very well and that a plane-wave cutoff of 400 eV is sufficient to achieve good convergence of the total energy; this cutoff is used throughout the present work. We have also tested these potentials on AgCl [18], pure Se and GaSe. In every case we find very good agreement with the experimental structure.

AIMD calculations on systems containing post-transition metals such as Ag are extremely demanding, because it is essential to include the *d*-electrons as valence electrons, and because

of the large plane-wave basis set needed to represent the d -orbitals. As a result, very few such AIMD simulations have been reported [19,20]. The present work relies heavily on parallel computation methods, and has been performed using the parallel *ab initio* code CETEP [21] running on a Cray T3D machine.

Our simulations of the Ag-Se liquid alloys have been performed on a system of 69 atoms in a cubic box with the usual periodic boundary conditions. We use Γ -point sampling, and a Fermi-smearing energy width of 0.2 eV. The Verlet algorithm is used to integrate the ionic equation of motion, with a time step of 3 fs. We have performed simulations at the temperature $T \simeq 1350$ K for three concentrations of $\text{Ag}_{1-x}\text{Se}_x$, namely: $x = 0.33$ (46 Ag atoms and 23 Se atoms), $x = 0.42$ (40 Ag atoms and 29 Se atoms) and $x = 0.65$ (24 Ag atoms and 45 Se atoms). The simulations are performed at a density which is linearly interpolated between experimental values for ℓ - Ag_2Se and ℓ -Se.

To initiate the simulations, we exploit the fact that an empirical pair-potential model [22] has been developed for the stoichiometric Ag_2Se system, which gives a reasonable reproduction of the liquid structure when used in classical molecular dynamics. We begin by making simulations with this empirical model, and we then switch over to AIMD and let the system equilibrate for a further 1 ps before collecting data over the next 2 ps. We reach the other $\text{Ag}_{1-x}\text{Se}_x$ compositions by replacing some of the Ag atoms by Se atoms and then equilibrating for 1 ps at the new composition; production runs of 2 ps are again performed in each case.

Fig. 1 shows the neutron-weighted static structure factor $S(k)$ obtained from our simulation for the Ag_2Se composition, compared with experimental data at $T = 1150$ K [1]. The overall agreement between theory and experiment is excellent, with all the main features having the correct position and magnitude. It is also remarkable that our simulation reproduces the position of the small pre-peak at wave vector $k \simeq 1.7 \text{ \AA}^{-1}$; its height, however, is lower than the experimental value. This discrepancy is probably due to the finite size of our simulation cell and the resulting lack of k -space resolution. Our simulation allows us to analyze the origin of the peaks in $S(k)$ in terms of the calculated partial structure factors

$S_{\text{Ag-Ag}}(k)$, $S_{\text{Ag-Se}}(k)$ and $S_{\text{Se-Se}}(k)$. We find that the main peak in $S(k)$ at $k \simeq 2.7 \text{ \AA}^{-1}$ is due to peaks in $S_{\text{Ag-Ag}}(k)$ and $S_{\text{Ag-Se}}(k)$, which reinforce each other. The pre-peak in $S(k)$ arises from a positive peak in $S_{\text{Se-Se}}(k)$ and a negative peak in $S_{\text{Ag-Se}}(k)$, which partially cancel each other. A more detailed analysis of the structure factors will be given elsewhere.

The partial pair correlation functions $g_{\text{Ag-Ag}}(r)$, $g_{\text{Ag-Se}}(r)$ and $g_{\text{Se-Se}}(r)$ for the three concentrations are displayed in Fig. 2. The results show that increase of Se content causes dramatic changes in $g_{\text{Se-Se}}(r)$. As Se content increases, a short-distance peak builds up. At stoichiometry, $g_{\text{Se-Se}}(r)$ exhibits broad peaks at 3.99 and 4.83 Å, and only a very weak tail below 3.0 Å. For $x = 0.42$, instead of a tail, there is a short-distance peak at 2.35 Å. The position of the main peak has shifted to 4.72 Å and has decreased in magnitude. The peak around 4.0 Å seen at stoichiometry has merged with the main peak to give rise to a shoulder. At the last concentration, the short-distance peak is dominant and $g_{\text{Se-Se}}(r)$ shows little structure beyond 4.0 Å with a low and broad second peak. We note that the radius 2.35 Å associated with the short-distance peak is very close to the Se-Se covalent bond length in crystalline and liquid Se [23]. The growth of the short-distance peak can be characterized by the Se-Se coordination number within a sphere of radius 3.0 Å, which we calculate to be 0.1, 0.71 and 1.7 for $x = 0.33$, 0.42 and 0.65 respectively. By contrast with the major changes in $g_{\text{Se-Se}}(r)$, the other two correlation functions change rather little with composition.

More insight into the structural changes can be gained from ‘snapshots’ of the ionic positions at the three concentrations (Fig. 3). To aid the eye, bonds have been drawn between Se atoms separated by less than 3.0 Å. As expected from the results for $g_{\alpha\beta}(r)$, the major feature is the formation of Se clusters as x exceeds 0.33. Already at $x = 0.42$, the Se atoms bond not only into dimers but also into larger Se_n clusters. At this composition, only $\sim 48 \%$ of the Se atoms are bonded, 76 % of the bonded atoms being one-fold coordinated and 22 % two-fold, the remaining 2 % having higher coordination. The dominance of one-fold and two-fold coordination means that most of the clusters are either dimers or Se_n chains.

At the composition $x = 0.65$, most of the Se atoms are in clusters, with only 7 % being isolated. The proportions of bonded Se in one-fold and two-fold coordination are now 35 % and 40 %, with a non-negligible 15 % being three-fold coordinated. The liquid is thus composed of one-dimensional Se_n chains interconnected *via* three-fold coordinated atoms, as shown in Fig. 3c. The Se_n clusters at this composition are large, with n typically > 20 .

The structural changes are intimately linked to the electronic structure. The calculated electronic density of states (DOS) and the local DOS on Ag and Se atoms for the three compositions are shown in Fig. 4. The main features are Se(4s) states at -12 eV, Ag(4d) states at -4 eV and Se(4p) states in the region above -7 eV; Ag(5s-p) states extend upwards from roughly the Fermi level E_F , and there is a significant hybridization between these and the Se(4p) states. The Se(4p) band of states stands out clearly from other parts of the DOS at all three compositions. For Ag_2Se , E_F lies in a pseudo-gap at the top of this band; the number of occupied 4p states per Se atom is equal to 3, and a partially ionic model approximating to Ag_2^+Se^- is appropriate. As x increases beyond 0.33, the number of occupied 4p states per Se atom falls below 3, and we attribute this to the formation of unoccupied anti-bonding 4p combinations associated with clusters. These anti-bonding states are hybridized with Ag(5s-p) states, and only become clearly visible at $x = 0.65$. We also note that with increasing x the Se(4s) band broadens strongly, and we can show that this arises from the formation of bonding and anti-bonding Se(4s) combinations in the clusters.

Our analysis of the structure and the DOS thus leads to a simple approximate picture of liquid Ag-Se alloys. At the Ag_2Se composition, the system consists approximately of isolated Ag^+ and Se^- ions. Our picture is that as the Se content increases, chain-like Se_n clusters are formed, and the system consists of a mixture of Ag^+ , Se^- ions and $(\text{Se}_n)^-$ complexes. As confirmation of this picture, we can use charge-balance arguments to estimate the number of Se-Se bonds at any composition. If the system consisted entirely of Ag^+ and Se^- ions, the net charge on a system of N_{Ag} and N_{Se} ions would be $N_{\text{Ag}} - 2N_{\text{Se}}$. If the clusters are all $(\text{Se}_n)^-$, the formation of every Se-Se bond reduces the charge by two units. For

electroneutrality, the number of bonds must therefore be $N_{\text{Se}} - \frac{1}{2}N_{\text{Ag}}$ and the coordination number of the short-distance peak in $g_{\text{Se-Se}}(r)$ must be $2 - N_{\text{Ag}}/N_{\text{Se}} = 3 - 1/x$. This gives predicted values of 0, 0.62 and 1.46 for the selenium-selenium coordination number at the three compositions, which are quite close to the values 0.1, 0.71 and 1.7 reported above. There are experimental indications for the occurrence of complex ions in other chalcogenide-metal alloys, for example $(\text{Se}_2)^=$ pairs in CuSe [24] and $(\text{Te}_n)^=$ chains in the Te rich side of K-Te [25].

In view of the dominant structural rôle played by Se_n clusters, the dynamics of their formation and dissolution is of great interest. We have performed a statistical analysis on the lifetime of Se-Se bonds, which shows that under the conditions we have studied they have a very short half-life on the order of 0.5 ps. A striking effect that seems to be linked with this is that the Se diffusion coefficient increases with increasing Se content. Details of these dynamical effects will be described elsewhere.

In conclusion, we have performed AIMD simulations on the liquid Ag-Se system to investigate how the atomic ordering and electronic structure evolve with composition in this typical alloy between metallic and semiconducting elements. The close agreement with neutron-diffraction data confirms the realism of the simulations. We have shown that the formation of chain-like Se_n complexes begins as soon as the Se content exceeds the stoichiometric value, and that the covalent Se-Se bond-length is very close to its value in crystalline and liquid Se. The concentration of Se-Se bonds and the changes of electronic structure can be understood using a simple ionic model in which the liquid is a mixture of Ag^+ , $\text{Se}^=$ and $(\text{Se}_n)^=$ ions. Although the Se_n complexes are structurally so important, individual Se-Se bonds are extremely transient, with a lifetime of less than a picosecond.

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FIGURES

FIG. 1. The total neutron weighted structure $S(k)$ factor of Ag_2Se . Solid line and circles represent simulation and experimental results [1] respectively.

FIG. 2. Partial radial distribution functions $g_{\alpha\beta}(r)$ of $\ell\text{-Ag}_{1-x}\text{Se}_x$ at concentrations $x=0.33$ (full line), $x=0.42$ (dotted line) and $x=0.65$ (dot-dashed line).

FIG. 3. Snapshots of typical configurations of $\ell\text{-Ag}_{1-x}\text{Se}_x$ at concentrations (a) $x=0.33$, (b) $x=0.42$ and (c) $x=0.65$. Silver atoms are shown as black spheres, selenium atoms as gray spheres. Bonds are drawn between Se atoms with separation $< 3.0 \text{ \AA}$. Bonds to atoms in neighboring cells are represented with two-colored sticks.

FIG. 4. Density of states (solid curve) and local densities of states (LDOS) for Ag (chain curve) and Se (dotted curve) from simulations of $\text{Ag}_{1-x}\text{Se}_x$ at $x = 0.33, 0.42$ and 0.65 . For clarity, the scale used for the Se LDOS is four times that used for the Ag LDOS. The vertical dotted line marks the Fermi energy.







